GCxGC COUPLED TO FAST SCANNING QUADRUPOLE MS FOR TRACE ANALYSIS OF POPs

Kinet C, De Pauw E, Focant JF

CART, Mass Spectrometry Laboratory, Chemistry Department, University of Liège, Allée de la Chimie 3, B-6c Sart-Tilman, B-4000 Liège, Belgium

Abstract

The paper describes preliminary data for the use of comprehensive two-dimensional gas chromatography (GCxGC) coupled to fast scanning quadrupole mass spectrometry (MS) for the measurement of dioxins and PCBs in biological samples. Electron impact (EI) and negative chemical ionization (NCI) are used and evaluated in terms of quantification using isotope dilution.

Introduction

As an alternative to the complex reference gas chromatography coupled to isotope dilution high resolution mass spectrometry (GC-IDHRMS) approach, new analytical methods are explored. Based on our previous investigations on the use of comprehensive two-dimensional GC coupled to time-of-flight MS (GCxGC-IDTOFMS) for the measurement of POPs[1], we currently evaluate the capabilities of GCxGC coupled to fast scanning low resolution quadrupole MS (qMS). The qMS can scan at up to 50Hz when operating in selected ion monitoring (SIM), offering the required sampling rate for narrow GCxGC peak characterisation. This instrument offers both electron impact (EI) and negative chemical ionization (NCI) to produce ions in the source. Advantages of NCI are known for a long time in terms of PCB analysis but it often suffers of lack or reproducibility and can make ID measurement difficult because of the limited availability of target ions. Both ionizations methods are investigated to evaluate the potential advantage of using GCxGC and NCI with this specific instrumental setup.

Materials and Methods

Chemicals, consumables and samples

All information on solvents, sorbents, labeled standards, equipments, and quality control (QC) procedures can be found in previous reports[2,3]. QC samples consisted in beef fat fortified with PCDD/Fs and PCBs. The mean level was 2.9±0.18 pg TEQ/g fat for PCDD/Fs, 1.2±0.06 pg TEQ/g fat for NO-PCBs, and 0.33±0.16 pg TEQ/g fat for MO-PCBs. QC samples were stored at -20°C prior to analysis. QC sample sizes were 20 g.

Sample preparation

Procedural blanks (both instrumental and method) and quality control (QC) samples were analyzed for the investigation. Our "in-house" QC samples were directly dissolved in hexane and processed through the clean-up system. The clean-up and fractionation in sub-groups of analytes was performed by automated multi-sorbent (silica, alumina, and carbon-based) liquid chromatography (LC) using the Power-Prep System (FMS Inc.). Sizes of Teflon disposable columns are available elsewhere[3]. The total run time was 100 min, plus a preventive decontamination program of 15 min. The MO- and I-PCBs were isolated in 120 mL of hexane-dichloromethane (1:1) and the PCDD/Fs and NO-PCBs were collected in 80 mL of toluene. Evaporation using a TurboVap II Workstation and a RapidVap was performed after addition of nonane as keeper. The final volumes were 90 µL for the MO- and I-PCBs fraction and 5 µL for the PCDD/Fs and NO-PCBs fraction. 5 µL of syringe (recovery) standards were added to the

GC vials prior to injection. All samples were analyzed by GC-IDHRMS[3] to produce reference values for comparison purposes.

GCxGC

The GCxGC hardware was the Zoex Loop Modulator (ZX1 - LN_2 Cooled Loop Modulation GC x GC System, Zoex Corp., Houston, USA). The simple setup is illustrated in Figure 1.

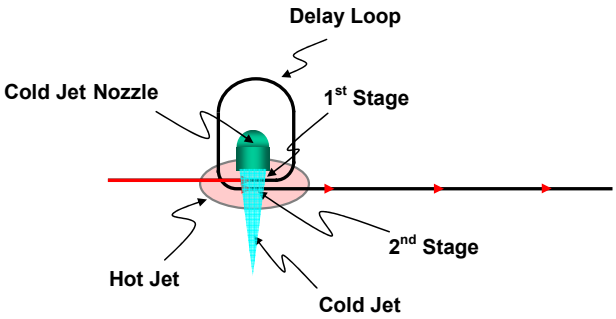

Figure 1: Schematic of the Loop Modulator (Source: Zoex Corp.).

The modulator was mounted on the Shimadzu GC oven and liquid nitrogen was used to create the cold jets. The column set was made of a 30m STX-500 (0.25 mm ID x 0.15 µm df) (Restek Corp.) in the first dimension (^{1}D) and either a 2m Rxi-17 (0.18 mm ID x 0.18 µm df) (Restek Corp.) or a 2m BPX-50 (0.10 mm ID x 0.10 µm df) (SGE) in the second dimension (^{2}D). The modulation period (P_M) was 4s. The hot pulse duration was 375ms. Helium was used as the carrier gas at a constant flow rate of 1.2 ml/min. 1.0 µl of the final extract in nonane was injected into a split/splitless injector held at 275 °C in splitless mode. The primary oven was programmed as follows: 140 °C for 2min, at 15 °C/min to 220 °C, at 7.5 °C/min to 250 °C, at 2 °C/min to 265 °C, at 28 °C/min to 320 °C for 5min. No secondary oven was used. The modulator temperature offset was 60 °C.

Quadrupole MS

The MS was the Shimadzu QP2010 Plus (Smimadzu, Duisburg, Germany). The MS transfer line temperature was 300 °C. The ion source temperature was 220 °C with an EI energy of 70eV. For SIM data acquisition, 4 masses (2 natives and 2 labels) were collected for each chlorination level. The scan rate was 25 Hz and the detector voltage was 1400V. For full scan data acquisition, the collected mass range was 30–500amu. The scan rate was 18 Hz and the detector voltage was 1100V. NCI was performed using methane as reagent gas. Data processing and display of the GCxGC chromatograms were achieved using both Shimadzu GCMS Solution software version 2.53 and GC Image software (Zoex Corp.), version 1.9. The quantification was performed in Excel spreadsheets after exportation of area measurements from GCMS Solution software.

Results and discussion

The stability of MS system was first investigated in regular GC to estimate the repeatability of measurements. A mass calibration tune was performed regularly and did not show any significant deviation over time. A selected standard solution injected twice a week for one month did show good response stability (Figure 2).

All GCxGC parameters were optimizes to reproducibly produce narrow ^{2}D peaks. Three to four slices per peak were obtained for all analytes. The classical peak width in ^{2}D was 600ms. This resulted in a number of 10-15 scans across each slice and a good description of the peak shape for the scan rates that were used. Spectral quality of this scanning

instrument is good and allows proper quantification performances. Typical scanning MS mass skewing was observed across GC peaks but did not affect the quantification.

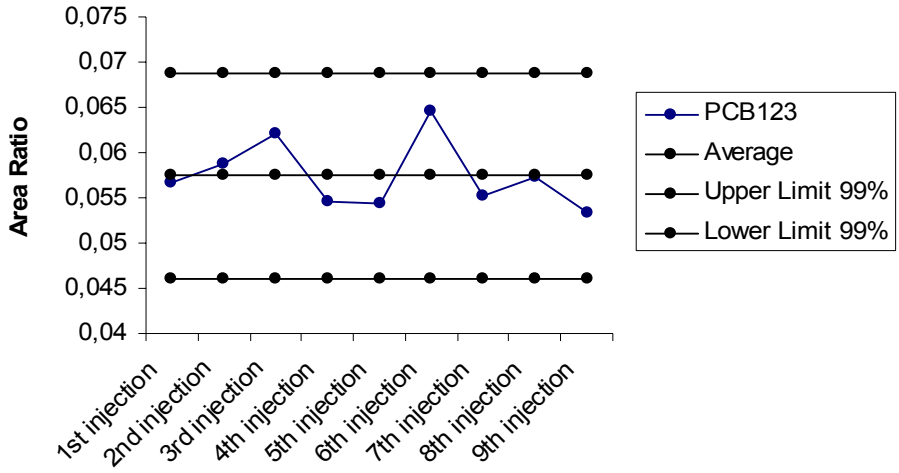

Figure 2: Stability of the ion ratio for 1pg native solution over one month period.

When using both EI or NCI, isotope dilution quantification can be performed under good QA/QC criteria. For quantification, the two most intense ions for the natives and the two most intense ions for the label were followed. This permitted a maximum scan rate of 25 Hz. Calibration curves were established the same way we do for the accredited GC-IDHRMS method. Ion ratios were checked and showed to be within a 20% range from theoretical ratios for both EI and NCI. Good correlation coefficients were obtained.

Figure 3 illustrates the GCxGC-NCI-qMS slice cluster corresponding to hexa-chlorinated PCB with a focus on PCB-156 and showing traces for the four monitored ions extracted from collected full-scan data.

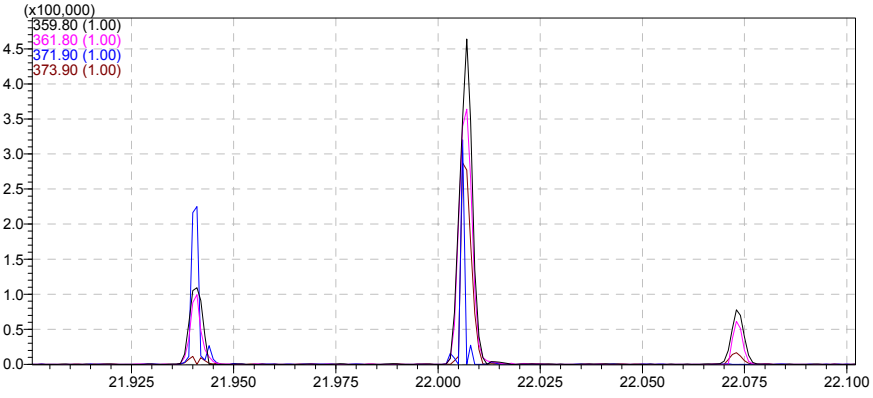

Figure 3: GCxGC peaks based on specific ions extracted from full-scan data.

Preliminary quantification data show good correlation with reference GC-HRMS data. QC charts testify for the good correlation between reference values and GCxGC values on a total MO-PCB TEQ basis (Figure 4).

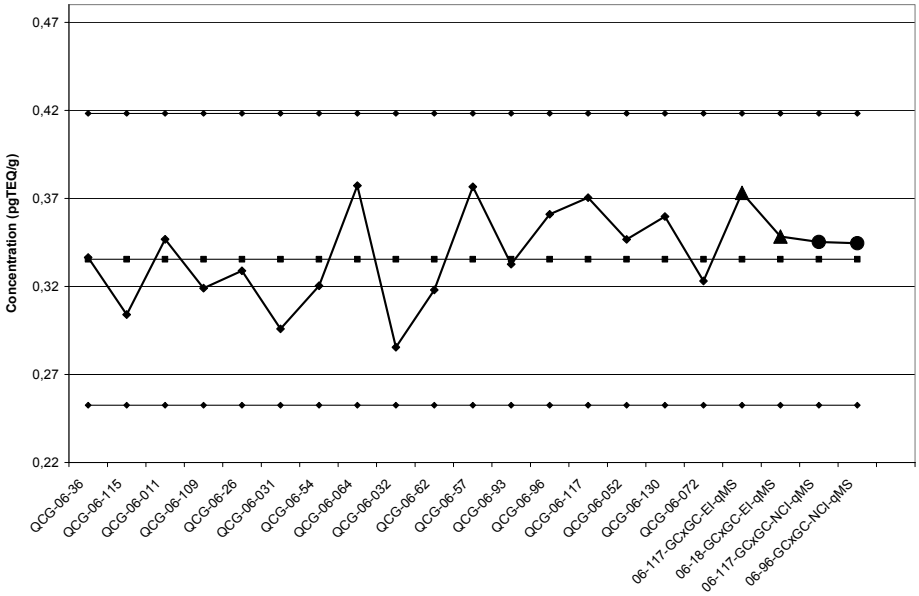

Figure 4: QC chart for MO-PCBs in GC-IDHRMS (Triangle are GCxGC-EI date, Ball are GCxGC-NCI data).

The use of NCI has the advantage of increasing the sensitivity. The same S/N ratio (S/N = 150 for the higher peak of the cluster for 1 pg injected) were obtained for SIM GCxGC-EI-qMS and for full-scan GCxGC-NCIqMS. Performing SIM GCxGC-NCIqMS would definitely yield to low pg sensitivity. For NCI runs, we actually had to lower the detector voltage to avoid saturation for some congeners. The injection volume was then f increased to 2 µl or the standards to ensure proper signal. A potential issue with NCI is however the low intensity of parent ion cluster for low chlorination level. This obviously makes ID quantification more delicate or even impossible in some extreme cases. As illustrated in Figure 5, quantification based on parent ions was only possible from penta-chlorinated to higher level of chlorination. A complete optimization of the ionization parameters (source temperature, reagent gas, gas pressure, …) is under consideration to optimize mass spectral quality and estimate if ID can still be performed in good conditions.

Nevertheless, those preliminary results encourage us to pursue in this direction and fully optimize SIM GCxGC-NCIqMS to attempt a validation study for quantification of PCBs and dioxins in biological samples.

References

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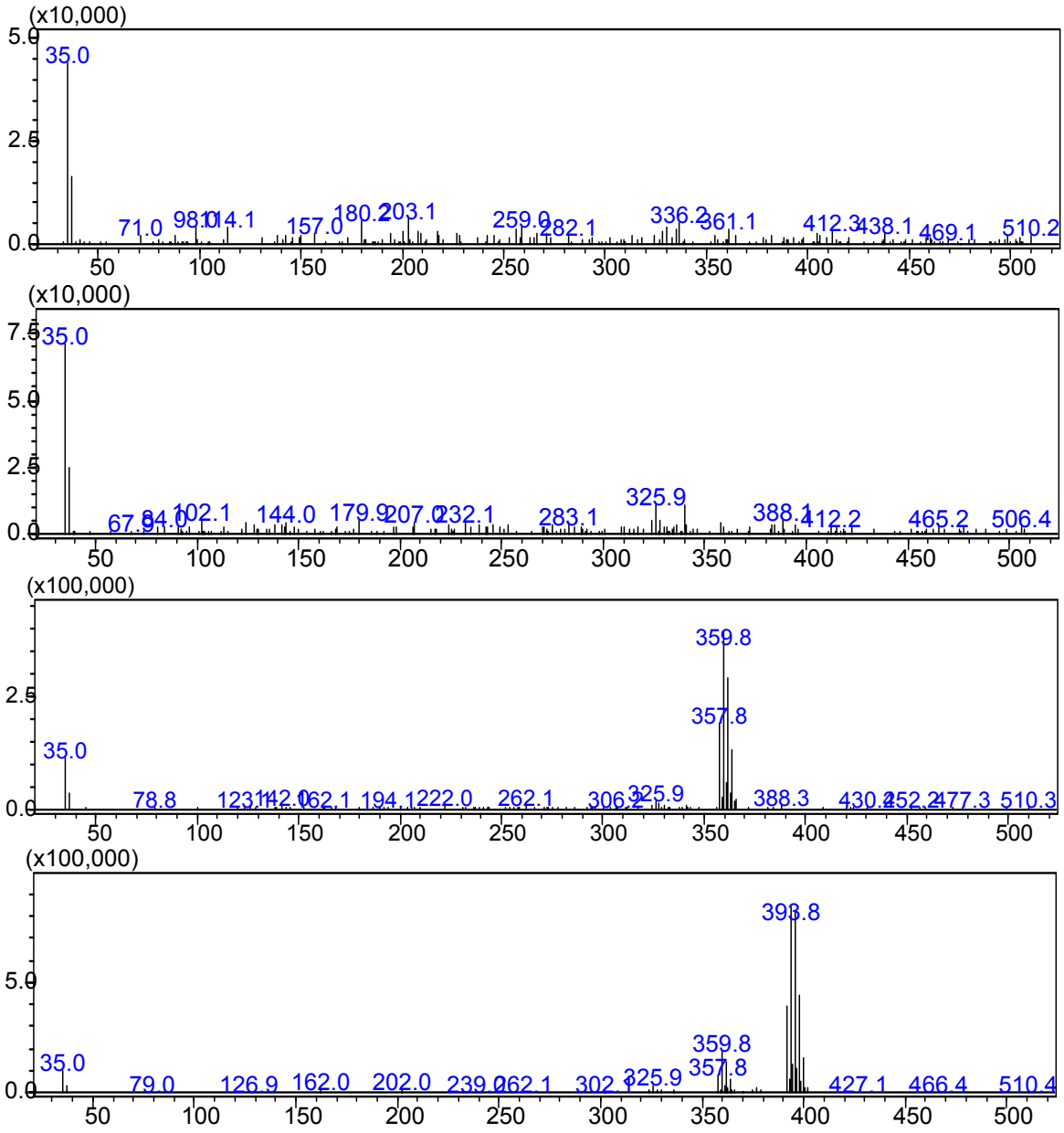

Figure 5: NCI (methane) mass spectra for different chlorination of PCBs (from top to bottom: tetra, penta, hexa, hepta).